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Rec'd PCT/PTO 17 MAR 2005

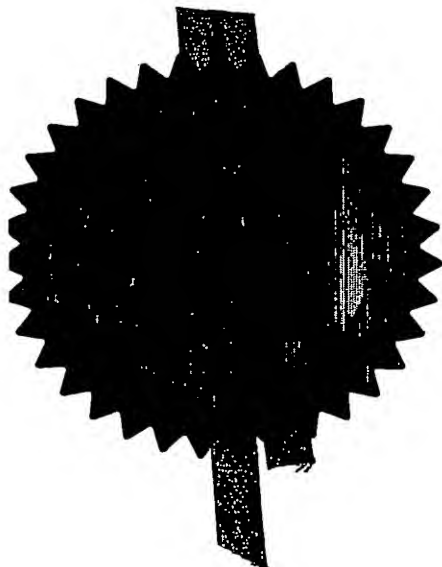
I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that the application is now proceeding in the name as identified herein.

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Signed

Andrew Gasey

Dated

16 September 2003

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GB 0221489.8

----- By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of -----

JOHNSON MATTHEY PLC,
2-4 Cockspur Street,
Trafalgar Square,
LONDON,
SW1Y 5BQ,
United Kingdom

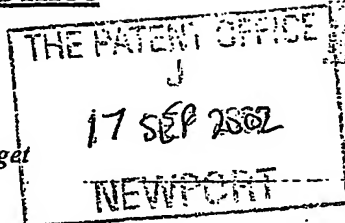
Incorporated in the United Kingdom,

[ADP No. 08519803001]

Patents Act 1997
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17SEP02 E748729-1 D02877
P01/7700-0-00-0221489-8



The Patent Office

Cardiff Road
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Gwent NP9 1RH

Request for grant of a patent

(see the notes on the back of this form. You can also get an explanatory leaflet from the Patent office to help you fill in this form)

1	Your reference	SYN 51074	
2	Patent application number (The Patent Office will fill in this part)	0221489.8	
3	Full name, address and postcode of the or of each applicant (underline all surnames)	IMPERIAL CHEMICAL INDUSTRIES PLC 20 Manchester Square, London W1U 3AN	
	Patents ADP Number (if you know it)		
	If the applicant is a corporate body, give the country/state of its incorporation	United Kingdom	
4	Title of the invention	SELECTIVE HYDROGENATION PROCESS	
5	Name of Your Agent (if you have one)	GIBSON, Sara Hillary Margaret	
	"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	Synetix Intellectual Property Department PO Box 1, Room N101 Belasis Avenue Billingham Cleveland England, TS23 1LB	
	Patents ADP Number (if you know it)	7912454004	
6	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or each of these earlier applications and (if you know it) the or each application number	Country	Priority Application number (if you know it)
			Date of Filing (day / month / year)
7	If this application is divided or otherwise derived from an earlier UK application, give the number and filing date of the earlier application	Number of earlier application	Date of Filing (day / month / year)
8	Is a statement of inventorship and of right to grant of a patent required in support of this request?	Yes	
	<p>Answer yes if:</p> <p>a) any applicant named in part 3 is not an inventor, or</p> <p>b) there is an inventor who is not named as an applicant, or</p> <p>c) any named applicant is a corporate body.</p> <p>See Note (d)</p>		

SECTION 30 (1977 ACT) APPLICATION FILED
12/12/02

Selective Hydrogenation Process

The present invention concerns selective hydrogenation processes and catalysts for use in such processes. In particular the invention concerns selective hydrogenation of aldehyde groups to alcohols in the presence of compounds containing olefin groups.

In the well-known processes for the production of alcohols by the so-called oxo process, an olefin is converted to an aldehyde by hydroformylation with carbon monoxide and hydrogen in the presence of a catalyst, which is typically a cobalt or a rhodium-based catalyst. The aldehyde is then hydrogenated over a copper-containing catalyst to give an alcohol which is purified by distillation. This process is often described as a two-stage oxo process because hydroformylation and hydrogenation are carried out in separate process stages. The hydroformylation product typically contains some unreacted olefin which may be removed from the process stream, normally by distillation, either before the hydrogenation or afterwards. The unreacted olefin may be returned to the hydroformylation stage either as a continuous recycle, or, more commonly and efficiently, as a separate feed stream on a campaign basis, i.e as a discontinuous recycle. The oxo-process is described in various texts, for example in the Kirk-Othmer Encyclopaedia of Chemical Technology (John Wiley) 4th Edn (1991), Vol1, p.903 – 908.

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The reaction product from the hydroformylation step contains typically 80% aldehyde, the remainder being mainly unconverted olefin. When the unreacted olefin is not separated until after the hydrogenation of the aldehyde hydroformylation product, it is possible for the olefin to be hydrogenated to saturated paraffin products, which are of relatively low value. It is economically desirable to minimise the hydrogenation of olefin so that it can be separated and recycled to hydroformylation for conversion to additional aldehyde. For this reason it is preferred to use a hydrogenation catalyst which is selective for the hydrogenation of the aldehyde group but which does not catalyse to a significant extent the hydrogenation of the C=C double bond in the olefin materials. Catalysts based on copper with chromium and/or zinc have been described for this process, as for example in US-A-2549416 in which the use of such catalysts is described in detail.

US-A-4052467 describes a process for the reduction of oxo-aldehydes to alcohols over a Cu/ZnO containing catalyst in which the feed contains a high concentration of thiophene (e.g. 500 – 2000 ppm) or another ring-type sulphur compound. The reaction conditions are specified to be in the range of temperature 450 – 550 degrees F and a pressure of 800 – 1200 psig with a LHSV in the range 1.0 – 1.5 to ensure that the ring-type sulphur compounds in the feed do not decompose to sulphur or sulphur compounds which deleteriously affect the life of the catalyst.

According to the invention, we provide a process for the hydrogenation of a feed stream containing at least one aliphatic aldehyde compound and an olefin over a catalyst comprising a copper compound and a zinc compound, and optionally a catalyst support, 5 comprising the step of treating said catalyst with an organic sulphur compound.

According to a second aspect of the invention, we provide a process for the production of an alcohol, comprising the steps of:

- 10 (a) reacting an olefin feed with hydrogen and carbon monoxide in a hydroformylation reactor in the presence of a suitable hydroformylation catalyst to form a hydroformylation product stream comprising an aldehyde and unreacted olefin,
- (b) optionally treating said hydroformylation product stream to separate the catalyst from the remainder of the hydroformylation product stream,
- (c) vaporising said hydroformylation product stream and feeding the vapour together with 15 a source of hydrogen to a hydrogenation reactor containing a bed of a solid hydrogenation catalyst comprising a copper compound and a zinc compound, to form a hydrogenation product stream comprising an alcohol and unreacted olefin,
- (d) separating said hydrogenation product stream into at least an alcohols stream and a stream containing said unreacted olefin,
- 20 characterised in that the hydrogenation catalyst is treated with an organic sulphur compound before or during step (c).

We have found that the conversion of olefin to paraffin can be significantly reduced, without significantly changing the conversion of aldehyde to alcohol, by treating the hydrogenation 25 catalyst with an organic sulphur compound. The unreacted olefin is normally recycled to the hydroformylation step either directly or, more preferably as a separate feed stream. If fed as a discrete recycle stream, the olefin which is separated from the hydrogenation product stream is preferably stored and then fed to the hydroformylation reactor as a distinct campaign so that the process conditions in the hydroformylation reactor may be 30 optimised for the olefins contained in the recycle stream.

The treatment of the catalyst with an organic sulphur compound may be done either prior to or during the feeding of the aldehyde-containing feed stream to the catalyst.

The sulphur compound can be added to the olefin feed before carrying out the 35 hydroformylation in which case it is essential that the sulphur compound does not react under the conditions of hydroformylation, in particular it must not be a poison for the hydroformylation catalyst. Alternatively and preferably, the sulphur compound may be added to the crude aldehyde as it is fed to hydrogenation. It is preferred to treat the catalyst on-line, i.e. in situ in the hydrogenation reactor during the reduction of the catalyst

The exact process by which the catalyst activity is moderated is not fully understood but it is likely to involve the formation of a sulphide species on the surface of the copper.

If no treatment is carried out, a freshly reduced catalyst will convert up to 80% of the olefin

- 5 in the crude aldehyde to paraffin. After treatment with a sulphur compound, the olefin conversion may be reduced to less than 30% so that more olefin is available to be recycled, leading to more favourable process economics.

The following examples are for illustration only.

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EXAMPLE

- A charge (16 tonne) of PRICAT™ 29-2 Cu/ZnO catalyst available from Syntex, was reduced to the active form by treatment with a low concentration of hydrogen in nitrogen, initially at 190°C and a pressure of 50 barg increasing to 260°C and 100 barg as the
15 reduction neared completion.

- A mixed C9 olefin (nonenes) stream was hydroformylated to give a mixture containing C10 aldehyde, unconverted nonenes and by-products including nonanes and high boiling C20 compounds. The crude aldehyde was hydrogenated to give a crude C10 alcohol
20 (isodecanol) by passing it over the reduced hydrogenation catalyst in the presence of hydrogen at 250-270°C and 235 barg. The liquid feed rate was 20 m³/hour and the hydrogen rate was 90 000 m³/hour, the rate for the latter being expressed as at 20°C and atmospheric pressure.

- 25 Over the first six days on line a total of about 67 litres (15 gallons) of thiophene was added to the hydrogenation feed, equivalent to 1.7 kg S per tonne of catalyst. Over the next 10 days the olefin converted to paraffin was equivalent to 25% of the olefin in the feed. The residual aldehyde content of the crude alcohol product was less than 0.5% by weight.

30 COMPARATIVE EXAMPLE

A similar charge of catalyst, which was not treated with thiophene, gave 60-80% conversion of olefin to paraffin after 6 to 16 days on line. The residual aldehyde content of the crude alcohol was again less than 0.5% by weight.